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14. ABSTRACT

Fluorinated compounds are very special in that they are water and oil repellent, highly lubricative, incombustible, and chemically inert. Fluorinated silsesquioxanes have attracted considerable attention from material scientists. One route to a *perfluorinated* silsesquioxane would be via condensation of an alkynyltrialkoxysilane or alkynyltrihalosilane. In this work *perfluorinated* alkynyl silane monomer represented by the formula R_fSiX_3 [R_f = perfluoroalkyne group, $X = OC_2H_5$] was synthesized in 50% yield by nucleophilic addition of 1- perfluorooctynl magnesium bromide to the commercially available alkoxysilanes as the electophiles. Various solvents were evaluated for their suitability in the silylation of alkynylmagnesium bromide intermediate. The product formation and reactivity rate is a function of molar ratios of reactants used and solvent polarity.

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Synthesis and Characteization of a Novel Reactive Perfluorinated Alkynyl Silane Monomer.

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Fluorinated compounds are very special in that they are water and oil repellent, highly lubricative, incombustible, and chemically inert. Fluorinated silsesquioxanes have attracted considerable attention from material scientists. One route to a *perfluorinated* silsesquioxane would be via condensation of an alkynyltrialkoxysilane or alkynyltrihalosilane. In this work *perfluorinated* alkynyl silane monomer represented by the formula R_fSiX_3 [R_f = perfluoroalkyne group, $X=OC_2H_5$] was synthesized in 50% yield by nucleophilic addition of 1-perfluorooctynyl magnesium bromide to the commercially available alkoxysilanes as the electophiles. Various solvents were evaluated for their suitability in the silylation of alkynylmagnesium bromide intermediate. The product formation and reactivity rate is a function of molar ratios of reactants used and solvent polarity.

SYNTHESIS AND CHARACTERIZATION OF A NOVEL REACTIVE PERFLUORINATED ALKYNYL SILANE MONOMER

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Introduction

Fluorinated compounds are useful in organic chemistry because of their pharmaceutical, agrochemical, and materials science applications.[1, 2] There is growing interest in new synthetic routes to produce such materials as well as in gaining a better understanding of their reactivity. Fluorosilicone materials, containing long-chain fluoroalkyl groups, possess many useful properties found in both silicones and fluoropolymers.[3] Fluorosiloxanes typically exhibit excellent solvent-resistance, thermal stability, weathering properties, and wear resistance. They also have surface energy values as low as 7.0 mN/m[4]

The first practical synthesis of organosilanes was accomplished by Kipping in 1904 using a Grignard reaction.[5] For practical purposes, alkoxy- and chloro-silanes are the most convenient precursors to alkynylsilanes because an alkynyl Grignard or lithium reagent can easily displace a chloro or alkoxy group. The Grignard reaction with alkoxysilanes is very general and found to be more selective than analogous reactions with chlorosilanes.[6] This results from stepwise substitution at the silicon atom. Substitution can be controlled by variation in reagent ratios as well as reagent reactivity. Multiple substitutions are favored when the activation energy for sequential substitution varies over a narrow range.[7] It has also been shown that the replacement of diethyl ether by toluene significantly accelerates the reaction of alkylmagnesium halides with alkoxysilanes, while no effect has been found for the same reaction with chlorosilanes.[8]

Fluorinated silsesquioxanes have attracted considerable attention in materials science.[9] Condensation of an alkynyltrialkoxysilane or alkynyltrihalosilane is a potential route to a the synthesis of a *perfluorinated* silsesquioxane. Therefore, a method was devised to produce a previously unreported perfluoroalkynyltriethoxysilane. The stability of the alkynyl-silcon bond under condtions of hydrolysis will determine if it is possible to produce the desired fluorinated polyhedral oligomeric silsesquioxanes or silsesquioxane networks.[10] Such materials would be of interest as surface property modifiers to a host of polymeric systems.

Experimental

Instrumentation. [1]H, ^{13}C, ^{19}F, and ^{29}Si NMR Spectra were obtained on a Bruker 300 or 400 MHz spectrometer using 5 mm o.d. NMR tubes. $CDCl_3$ and C_6F_6 were used as the internal reference standards ([1]H: $CHCl_3$ at 7.26 ppm; [13]C: $CDCl_3$ at 77.00 ppm; [19]F: C_6F_6 at -163.8 ppm). External tetramethylsilane at 0 ppm was used for [29]Si.

Materials. 1H-Perfluorooct-1-yne and hexafluorobenzene were purchased from Synquest Laboratories and used without further purification. Ethylmagnesium bromide solution, tetraethyl orthosilicate (TEOS), tetrachlorosilane, and chlorotriethoxy silane were purchased from Aldrich Chemical Co. Anhydrous diethyl ether, THF, and toluene (Aldrich) were dried by passage through columns of activated alumina under a nitrogen atmosphere. The solvents were degassed prior to use. All reactions were carried out under an inert atmosphere of dry N_2 unless otherwise stated in the procedure. All manipulations of compounds and solvents were carried out using standard Schlenk line techniques.

Synthesis of triethoxysilylalkyne: A solution of ethylmagnesium bromide (5 mmol) in 5 mL of anhydrous THF was taken in an addition funnel and slowly added to a stirring solution of 1H-perfluorooctyne (5 mmol) in anhydrous ethereal solution. The reaction was allowed to stir for approximately 2 h at ambient temperature and canulated into a stirring solution of tetraethyl orthosilicate (15 mmol) in ethereal solvent. The above mixture was stirred overnight. The solvent was removed in vacuo from the reaction mixture and product extracted using hexafluorobenzene and filtration through celite. After removing all volatiles under a dynamic vacuum, the yellow colored filtrate was transferred to a distillation flask. The product, perfluoro-1-octynltriethoxysilane was obtained by fractional distillation under reduced pressure as a colorless liquid in 50% yield. ^{19}F NMR (C_6F_6) δ -80.89 ppm (3F), -98.43 ppm (2F), -120.36 ppm (2F), -122.17 ppm (4F), -125.70 ppm (2F). ^{29}Si NMR δ -78.06 ppm

Results and Discussion

Traditionally, the synthesis of alkoxy silanes has been accomplished by the treatment of Grignard or organo-lithium reagents with either $SiCl_4$ (followed by alcoholysis),[11] $Cl-Si(OR)_3$[12] or $Si(OR)_4$[13] The use of $Si(OR)_4$ for the one-step preparation of alkoxysilanes *via* the organometallic approach has shown to have several advantages, including the commercial availability, low cost, and ease of handling and storage of tetraalkyl orthosilicates.[14] Treatment of alkynylmetalloids with this less reactive electrophile, $Si(OEt)_4$, favors the formation of monoalkynyl silanes because the alkoxide group is more difficult to displace from silicon than a chloride atom.[15] The drawback of using the more reactive $SiCl_4$ as the electrophile include the formation of tetrakis(perfluoroalkynyl)silane species and the two step conversion to alkoxy silane. Treatment of the alkynylmetalloid with $Cl-Si(OR)_3$ favored the formation of monoalkynyl silane by preferential displacement of chloride from silicon, however formation of inseparable di- and tri-alkynyl silanes also takes place. In this work, 1-perfluorooct-1-ynylmagnesium bromide was selected as the initial nucleophile to be investigated in the metalation procedure. Grignard reagents have been reported to have significantly lower reactivity than the lithium reagents, which rapidly decompose at ambient temperatures. The inexpensive, commercially available electrophile tetraethyl orthosilicate, chlorotriethyl orthosilicate and tetrachlorosilane were each evaluated for their efficacy in formation of the Si-C≡C moiety. Ether, THF, and THF/toluene were evaluated for their suitability in the silylation of alkynylmagnesium bromide intermediate.

Conclusions

In the current work, a novel fluorosilane monomer was synthesized *via* a Grignard reaction, followed by substitution between perfluorooct-1-ynyl magnesium bromide and alkoxysilanes. The product formation and reactivity rate is a function of molar ratios of reactants used and solvent polarity. It was determined that the substitution reactions can proceed efficiently and in a controlled manner when the solvent polarity is controlled. The reaction temperature did not influence the product yield, which is contrary to the chemistry of non-fluorinated analogues.

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